

## "PHOTOCONDUCTIVITY OF LEAD AZIDE"

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### Introduction

Evans and Yoffe<sup>(1)</sup> reported lead azide to be a weak photoconductor with the maximum in its spectral distribution occurring at about 3650Å. McLaren<sup>(2)</sup> reported the absorption edge to be 4000Å and that absorption at frequencies below this was due to residual carriers and could be used as an indication of the purity of the sample. In the photoconductivity experiments of McLaren and Rogers<sup>(3)</sup> the photocurrent for lead azide was found to increase at first rapidly, (but at a rapidly decreasing rate) to reach a saturation value after about 30 seconds illumination, the initial rise being produced by photoelectrons migrating toward the anode. With continued illumination the photocurrent decreased by exponential decay typical of a space charge limitation of the flow of electrons, owing to the immobility of positive holes;<sup>(4)</sup> after prolonged illumination the primary photocurrent leveled off at about 0.2 of the maximum. A linear relationship was found between the primary photocurrent and the electric field strength indicating that most of the photoelectrons were trapped before reaching the anode. Saturation of the photocurrent by increasing the electric field strength did not occur.

Dumas<sup>(5)</sup> studied the rate of photolysis (photochemical decomposition) of amorphous lead azide as a function of the spectral quality of the incident light and found the rate to be proportional to the intensity of illumination with peaks occurring at 2800Å and 2400Å. Photocurrents were obtained in partially decomposed samples, although they were detected in freshly prepared samples. The peaks at 2800Å and 2400Å were ascribed to two exciton bands. An F center was assumed to be formed from an exciton by the trapping of an electron at an anion vacancy. The positive holes from the dissociation of the excitons then supposedly diffuse to the surface and combine in pairs to form nitrogen gas.

Rate-time and rate-intensity curves in the photolysis of sodium, mercurous, and lead azide were reported by Dodd.<sup>(6)</sup> For lead azide the experimental quantum yield was determined to be 0.056, a value considered by Dodd to be a lower limit. The diffusion constant for photolysis was given as  $2 \cdot 10^{-17}$  cm<sup>2</sup>/sec. Dodd considered that the rate controlling step in photolysis might be the diffusion of some large entity,<sup>(9)</sup> and that this diffusion entity was perhaps molecular nitrogen formed along grain boundaries. The rate of migration of these molecules to the surface was thus considered to be diffusion controlled.

The purpose of the present investigation was to determine some of the factors that affect the photoconductive behavior of lead azide thereby augmenting the rather limited information presently available, to study the defect structure and solid state properties of lead azide through photoconductivity, and finally to determine possible relationships between photoconductivity and explosive sensitivity.

### Experimental Methods

Compressed pellets made either from especially-grown small single crystals or from commercial lead azide were used in this investigation. The single crystals were grown in the dark by a diffusion method which utilized the reaction of hydrazoic acid vapor on a lead nitrate solution.<sup>7,8</sup> Well-formed crystals approximately 5 mm long and 1 mm in diameter were grown by this method.

A special sample holder (Fig. 1) adapted to hold 1/4" and 1/8" pellets, held the pressed lead azide pellet under illumination. The sample holder was constructed of copper and mounted in a pyrex dewar flask to permit either cooling or warming the sample as well as evacuation to prevent oxidation of the sample surface. The lead azide pellet was mounted between silver electrodes electrically insulated from the copper block. Electrical connections were made by tungsten leads sealed through the pyrex dewar section. Quartz windows were used to permit transmission of ultra-violet light, the windows being placed on both sides of the assembly to permit light absorption measurements if desired. In experiments requiring monochromatic illumination the sample holder was mounted in a plastic block and placed in a Beckman DK-2 spectrophotometer. A Uvis Grating Monochromator obtained from the Farrand Optical Company with a range of 2200Å to 6500Å was also employed. Illumination was provided by an Osram HBO-200 high pressure mercury lamp Model 520-A. A Photovolt Corporation photometer was used to measure the intensity of the incident beam controlled by Kodak Wratten neutral density filters. The lead azide pellet was mounted in series with a decade shunt, which in combination with the electrometer formed a sensitive ammeter.

Under the influence of an electric field a small dark current was observed. This dark current was allowed to reach steady state, and the photocurrent was taken to be the increase in the current above this steady-state dark current when the sample was illuminated.

### Experimental Results

#### Photoconductivity vs. time, temperature, field strength:

Figure 2 presents curves showing the variation of photocurrent at 36°C, -80°C, and -195°C with time of illumination, utilizing the full output of the lamp and an electrical field strength of about 160 volts/cm. At 36°C the photocurrent continued to rise even after 200 seconds illumination. For the lower temperatures the photocurrent rose to a maximum value then under continued illumination dropped to a fraction of the maximum.

The drop in photocurrent may be attributed to a build up of space charge resulting from the decreased mobility at low temperatures of the positive holes created when electrons are raised to the conduction band. This space charge was removed by permitting the sample to warm up to room temperature and remain over night with no applied field. At elevated temperatures, however, the space charge disappeared much more rapidly. The photocurrents in general decreased as the temperature was lowered. The fact that in the example here a higher photoconductivity was recorded at  $-195^{\circ}\text{C}$  than at  $-80^{\circ}\text{C}$  was evidently due to differences in the history of the samples. In runs (c) and (d) which were essentially the same, the maximum photocurrent was only about one half that of run (b) indicating that space charge was still present to limit the current. There are some peculiar flat sections in curve (b) which were found to be reproducible in subsequent experiments.

The effect of the electric field strength on the photoconductivity of lead azide illuminated at  $4060\text{\AA}$  was determined by varying the applied voltage. The result was a linear relationship between photocurrent and the applied voltage which indicated that most of the photoelectrons were trapped before reaching the anode, a fact which precluded determination of the quantum efficiency.

The effect of sample thickness for illumination at  $4060\text{\AA}$  was investigated using  $1/8"$  diameter pellets containing 10, 15, 20, and 25 mg of colloidal lead azide. The dark current proved to increase with pellet thickness. This was the result of a greater number of electron donating centers present in the thicker pellets and the fact that the distance between electrodes remained constant at  $1/8"$ . The photocurrent, on the other hand, decreased with pellet thickness; the decrease was probably due to the fact that the number of electron traps increased with pellet volume (a bulk effect) but the region contributing photoelectrons remained constant since the photoelectrons were released in a thin surface layer on the illuminated side of the pellet. Because of this effect all runs (other than those involving the effect of sample thickness) were made using 20 mg pellets pressed to the same thickness.

Photocurrents vs. wave length of incident light and heat treatments:  
Typical curves of photocurrent against wave length for two pellets pressed from freshly dried, commercially prepared colloidal lead azide are shown in Fig. 3. The desired wavelength was set on the monochromator while the sample was shielded from the light. The pellet was then illuminated 10 seconds, which was sufficient time for the photocurrent to reach its maximum value, and the reading taken, the process being repeated in measurements at each wavelength. By far the most prominent peak fell at  $4060\text{\AA}$ , with smaller ones, somewhat difficult to resolve, located at  $3650\text{\AA}$ ,  $5400\text{\AA}$ , and  $5800\text{\AA}$ . The major peak at  $4060\text{\AA}$  fell beyond the absorption edge located at  $4000\text{\AA}$ . Photolysis occurs at  $3650\text{\AA}$  which is within the absorption band of lead azide but according to Dodd, et. al.,<sup>(6)</sup> would not occur for longer wavelengths. Therefore, the peak at  $4060\text{\AA}$  was not due to photolysis.

Interesting conductivity effects were found in partially decomposed samples obtained by heat treating lead azide at  $250^{\circ}\text{C}$  for varying lengths of time,

250°C being well below the (usual) "explosion" temperature of lead azide. Initially the heat treatment was conducted by plunging a small aluminum capsule containing 50 mg of lead azide into a molten metal bath of the desired temperature. The spectral distribution of the photocurrents after 5, 10, and 15 minutes of such treatment is shown in Fig. 4a, and in Fig. 4b, plotted on a different scale, are the photocurrents after 20, 30, and 40 minutes heat treatment. The increased photoconductivity in the 4060Å band is striking, this increase becoming particularly large with 20 to 40 minutes heat treatment.

The effect of more extended "aging" at 250°C on the photoconductivity in the 4060Å band was studied in order to determine whether the photoconductivity continued to increase, reached a maximum and then leveled off, or attained a maximum and then decreased. Samples of colloidal lead azide heated in shallow metal trays in a drying oven at 250°C for times ranging from 5 minutes up to 260 minutes showed a marked increase in the dark conductivity with time. However, it was impossible to measure the photocurrents against this high-dark current background. In Fig. 5 are plotted the maximum dark currents as a function of the time of heat-treatment, these maxima occurring as a rule 2 to 3 minutes after application of the electrical field. The highest dark current occurred after about 15 minutes heat treatment. After 40 minutes heat-treatment the dark current had leveled off in time at a level considerably below this value. An electric field strength of 1575 v/cm was sufficient to destroy nearly all the available centers providing photocurrent electrons. This is suggested by the fact that the photocurrent was negligible compared to the dark current. Heat-treating the lead azide at 250°C in shallow trays in a drying oven evidently had a different effect than treatment in the small aluminum capsules in the molten metal bath. The samples were apparently more efficiently exposed to the heat owing to the smaller (50 mg) and more shallow samples. The thermal conductivity of lead azide at 45°C and a density of 3.62 g/cm<sup>3</sup> is only  $4 \cdot 10^{-4}$  cal/cm<sup>2</sup> sec. C°/cm and thus the sample may not have heated efficiently in the former method.

Curve (b) of Fig. 5 was plotted from data obtained using the same pellets except that the dark current readings were taken after one minute exposure to the electrical field, at which time the maximum dark current had not as yet been reached, and curve (c) shows the results of a second run that was made in the same manner. The dark current was again a maximum after 10 to 20 minutes heat-treatment although in the re-runs the absolute magnitudes of current were lower. On the following day the pellet that had been heat-treated for 15 minutes was re-run. Before the dark current had leveled off it was illuminated at 4060Å and exhibited an increased current flow. When illumination was discontinued, a characteristic exponential decay of current was observed. The dark current, however, continued to increase. Upon re-illumination the electrometer pointer began to oscillate, and the sample suddenly detonated. Another pellet heat-treated 20 minutes was mounted in the holder and the electric field applied carefully. The dark current reading built up and went off scale on the 10<sup>-8</sup> ampere range, at which time the potential was removed quickly to avoid another explosion.

Colloidal lead azide was treated in a similar manner at 100°C. In this case, photocurrents were measurable above the dark current background. The

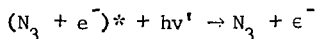
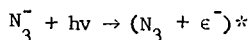
photocurrent in the 4060Å band and the dark current are shown in Fig. 6 as a function of the time of heat treatment. Maximum values corresponded again to treatment times in the 10 to 20 minute range.

Storage in different gases: The effects on photoconductivity in the 4060Å band of extended storage at 35°C in nitrogen, oxygen, air, carbon dioxide, and argon were investigated using samples prepared by Hong.<sup>(10)</sup> The colloidal lead azide was placed in pyrex test tubes wrapped with black tape so as to be light tight. The test tubes were mounted in a rack inside a box controlled at 35°C, and dried gases were passed at a constant rate of flow through the samples. Samples were removed at desired intervals and the lead azide content, sensitivity to light, ignition, and photoconductivity determined. The photoconductivities are shown in Fig. 7. Treatment times were continued to 80 days for nitrogen, air, oxygen, and argon and 28 days for carbon dioxide. Surprisingly, a large increase in photoconductivity was observed for samples stored in nitrogen. Storage in air and oxygen produced much smaller increases, while storage in argon appeared to lower the photoconductivity. The exposure in carbon dioxide was not sufficiently long to establish a definite trend. Measurements were usually made immediately after the samples had been removed from the treatment box. However, the points marked 1 and 2 are the values obtained for samples that had been treated in the nitrogen atmosphere for 65 and 80 days respectively, and then rerun for photoconductivity after having been stored in the dark in a sealed, hard rubber container at ambient conditions for about 6 weeks and 4 weeks respectively. The photocurrents were significantly diminished as a result of such storage in air indicating a decrease in the number of electron donating centers in the sample. In order to determine more definitely if the number of centers could be influenced in this way, new samples that had been treated 65 and 80 days in nitrogen at 35°C were placed in a vacuum oven at 100°C for 4 hours (with points 3 and 4 resulting) and for 16 hours (points 5 and 6). The photocurrents were thereby reduced to much lower values.

### Discussion

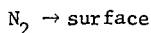
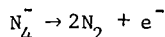
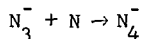
By far the most important band in the spectral distribution of the photoconductivity of colloidal  $\alpha$ -lead azide fell at 4060Å. Other bands located at 3650Å, 4300Å, 5400Å, 5800Å were much less prominent, but definitely real because they proved to be reproducible except for the band at 4300Å observed only in a sample that had been heat-treated for 15 minutes at 250°C (see Fig. 4a). These bands should correspond to the absorption spectrum of lead azide which, has not yet been measured because of technical difficulties. A recent development by Head<sup>(11)</sup> for producing extremely thin films and micro-crystals of lead azide may, however, permit such absorption measurements. The observed bands in the spectral distribution of  $\alpha$ -lead azide are evidently due to the ionization of centers that can release electrons into the conduction band. These centers may be F, F', V<sub>1</sub>, R, M, colloidal or exciton types.

The 3650Å band is believed to be due to the ionization of excitons formed in the photolytic decomposition of lead azide which may be represented as follows:



The result is the formation of a positive hole and a conduction electron, the former being immobile at low and mobile at high temperature.

The 4060Å band is by far the most prominent one in the photoconductivity spectrum of  $\alpha$ -lead azide. It is not associated with photolysis because photolysis occurs only for wavelengths shorter than the absorption edge at 4000Å. The 4060Å band was strongly affected by heat treatment and by storage in nitrogen gas. For these reasons it is believed to be due to  $V_1$  centers (interstitial nitrogen atoms). The enhanced photoconductivity resulting from the nitrogen environment indicates that the nitrogen molecules absorb on the lead azide surface, some of them dissociating into nitrogen atoms, eventually finding their way into interstitial positions in the lead azide lattice to promote photoconductivity. Since photoconductivity in lead azide may be largely a surface phenomenon, it is possible that the nitrogen atoms need not diffuse far into the lattice. The fact that the dark conductivity, which is a bulk effect, was also increased indicates, however, that considerably more than a thin surface layer may be involved. The size of nitrogen atoms and molecules and the lattice parameters of lead azide do not prohibit the possibility of diffusion into the lattice. The decomposition of lead azide with the evolution of nitrogen at surface and internal defects of the crystal should also contribute to the formation of the  $V_1$  center. Indeed some of the enhancement in photoconductivity by heat-treatment may be due to this effect. These  $V_1$  centers contribute to the photocurrent by the following mechanism:



Nitrogen molecules could dissociate and enter the lattice forming more  $V_1$  centers or diffuse to the surface and escape. The latter would explain the diffusion constant reported by Dodd.<sup>(6)</sup> The presence of the  $N_4^-$  radical has been confirmed by Shuskus, et. al.,<sup>(12)</sup> in potassium azide; it was reported to be a linear configuration stable only at low temperatures. This configuration has been discussed also by King and Coworkers<sup>(13)</sup> in studies of sodium azide.

Of particular interest is the fact that a maximum in the dark conductivity against time curve occurred at about 10 to 15 minutes treatment at 250°C and at 100°C. It is surprising that the maximum for samples aged at 100°C occurred at

about the same time as samples aged at 250°C indicating that at least two opposing effects are involved or the effect is a zero enthalpy and finite entropy one.

The origin of the 4300Å band is as yet unknown. It appeared only in a sample aged at 250°C for 15 minutes (see Fig. 4a). The centers producing this band may have an important bearing upon sensitivity because this particular sample was the one that detonated in the photoconductivity apparatus.

The 5400Å band had approximately the same intensity as the F band and may thus be associated with it in one way or another. One possibility is a  $\beta$ -band produced by an excited electron on an anion near an F center. Another possibility is an  $R_1$  center (two neighboring vacancies with an associated electron).

The 5800Å band is believed to be due to F centers, since this is the spectral region where F centers are usually located, and F centers were definitely present because the samples became colored under the effect of illumination. Electron micrographs of replicas of lead azide crystal surfaces<sup>(14)</sup> showed that lead azide decomposed by a semi-conductor mechanism, i.e., by a process involving the transfer of electrons. Decomposition is accompanied by the growth of lead nuclei on the crystal surfaces, primarily on the (010) face and electrons and/or excitons find their way to one of these nuclei which acts as an electron trap, charging the nucleus negatively whereupon the nucleus may then attract lead ions causing the continued growth of the nuclei during decomposition. Since the slow decomposition of lead azide occurs via an electron transfer process, the concentrations and types of active centers might be expected to influence the slow decomposition of lead azide and the consequent formation of a "hot spot" in the case of initiation of detonation.

A miniature card gap test for the sensitiveness of primary explosives to shock initiation similar to the standard test adopted for liquid monopropellants was developed at this laboratory.<sup>(16)</sup> It was applied to colloidal lead azide heat-treated for various lengths of time at 250°C,<sup>(17)</sup> the lead azide being taken from the same batches as those used in the photoconductivity measurements, in order to make a direct comparison of the sensitivity and photoconductivity results. In these tests the lead azide exhibited a maximum sensitivity at a treatment time of 15 minutes. A test for measuring the sensitiveness to initiation by light similar to the one developed by Eggert<sup>(18)</sup> was also applied to heat-treated lead azide,<sup>(10)</sup> and a maximum in the sensitivity was found to occur after 5 minutes heat-treatment. It is interesting to note that the times to sensitivity maxima fell approximately in the same range of heat-treatment times that yielded the maximum dark conductivity for aging at 250°C and the maximum dark conductivity and photoconductivity in the 4060Å band for aging at 100°C. Originally it was thought that the increased sensitiveness from heat treatment was due to autocatalytic action of the lead specks, although the appearance of the maxima after such short heat-treatment times when very little decomposition and lead speck growth had occurred was difficult to explain. The dark conductivity and photoconductivity results indicated, however, active centers other than lead specks must be produced by the heat-treatments.

The colloidal lead azide samples that had undergone (dark) storage at 35°C in various dry atmospheres were also subjected to the light ignition

test for sensitivity<sup>(10)</sup> after 26, 65, and 80 days. In the case of the nitrogen, air, and oxygen treatments the sensitivity was not found to be significantly different, and it did not appear to vary with the length of treatment. After 26 days in argon, however, the lead azide was somewhat less sensitive than the standard and after 65 and 80 days the sensitivity proved to be lowered considerably more. In view of the photoconductivity results with the same material (Fig. 7) a possible explanation for these results is that during the previous history of the sample exposure to the air was sufficient for the diffusion of nitrogen and possibly oxygen into the lead azide lattice to produce active centers probably of the  $V_i$  type. As far as these atoms were concerned the argon environment acted similar to a vacuum, reducing the partial pressure of nitrogen to zero and allowing the centers to diffuse from the crystal. In the case of lead azide stored in nitrogen, air, and oxygen additional active centers were formed as shown by the photoconductivity measurements; the increased number of centers, although easily detected by photoconductivity, were not sufficient to produce a significant change in sensitivity.

The above correlations suggest that one may eventually relate sensitivity to photoconductivity or possibly dark conductivity once the active centers are identified that exert the greatest effect upon sensitivity, and it is determined how these centers interact and how their concentrations alter the slow decomposition of lead azide.

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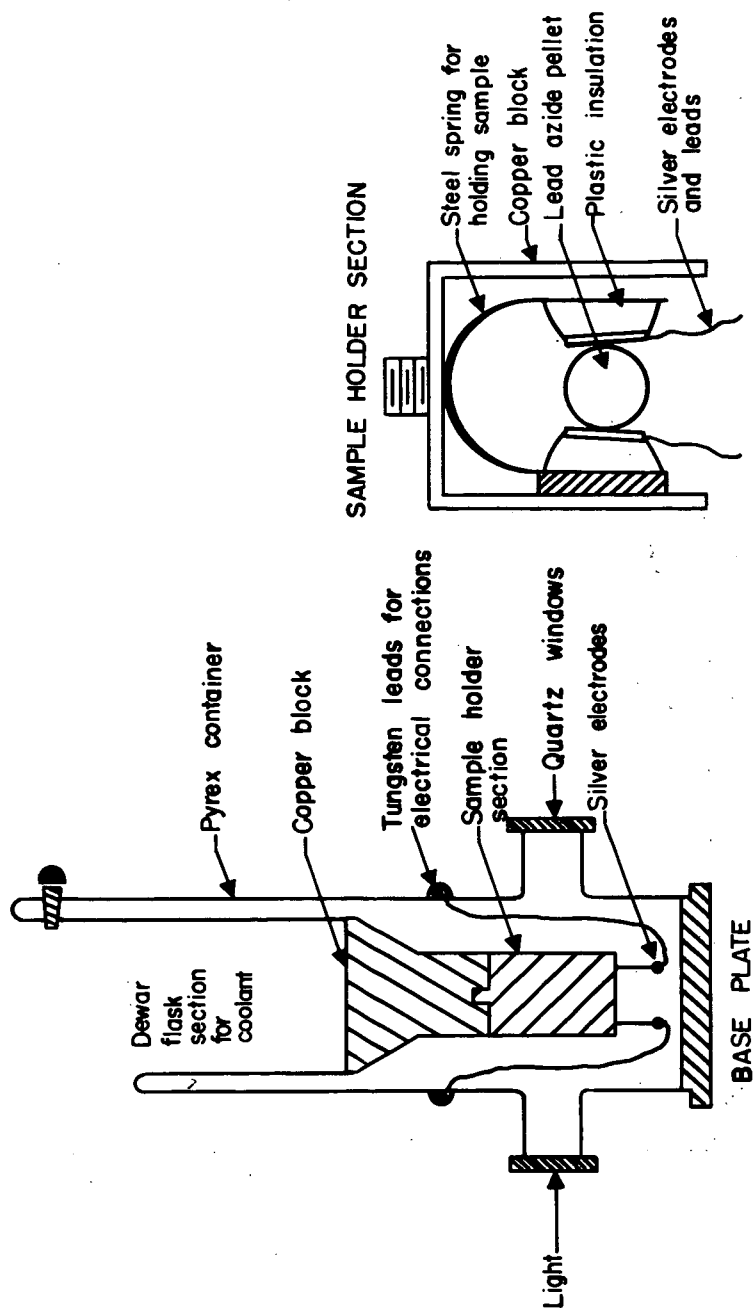


Figure 1. Sample holder used in the photoconductivity experiments.

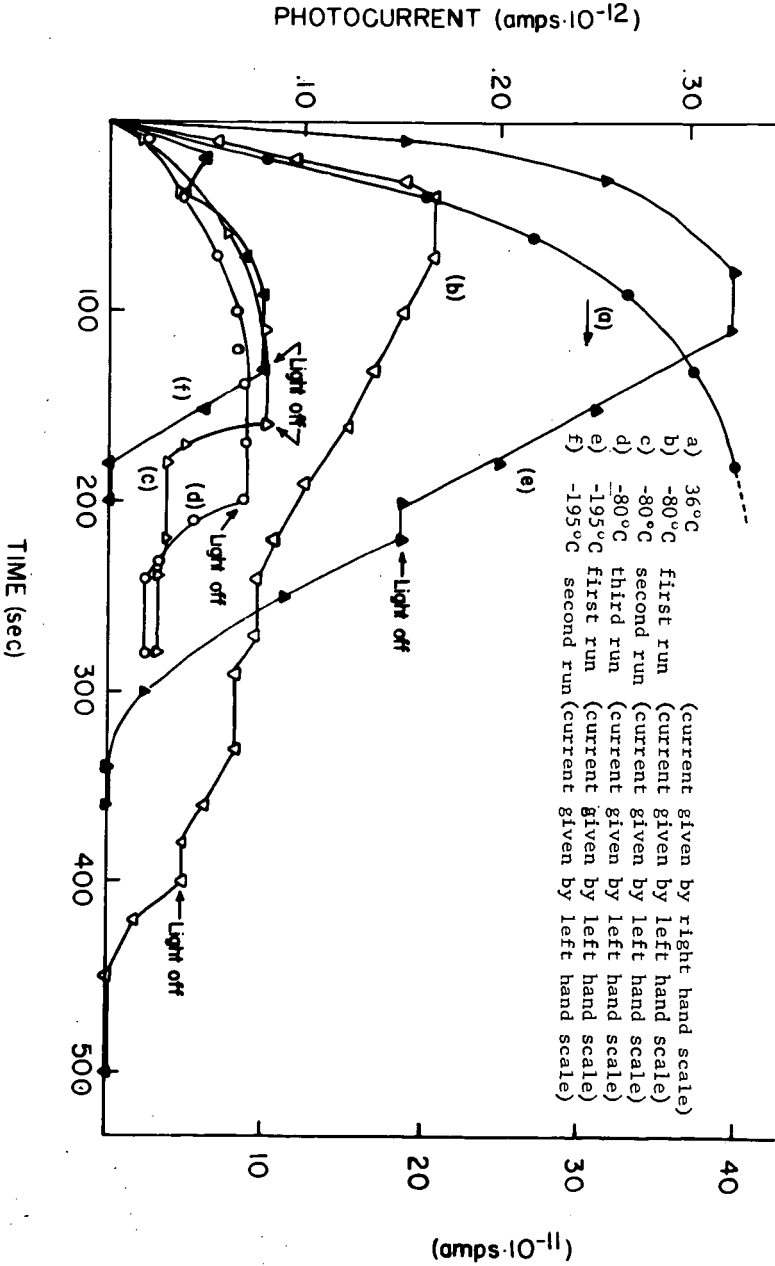


Figure 2. Photocurrent vs time for lead azide at various temperatures using the full output of the lamp and an electrical field strength of about 160 v/cm.

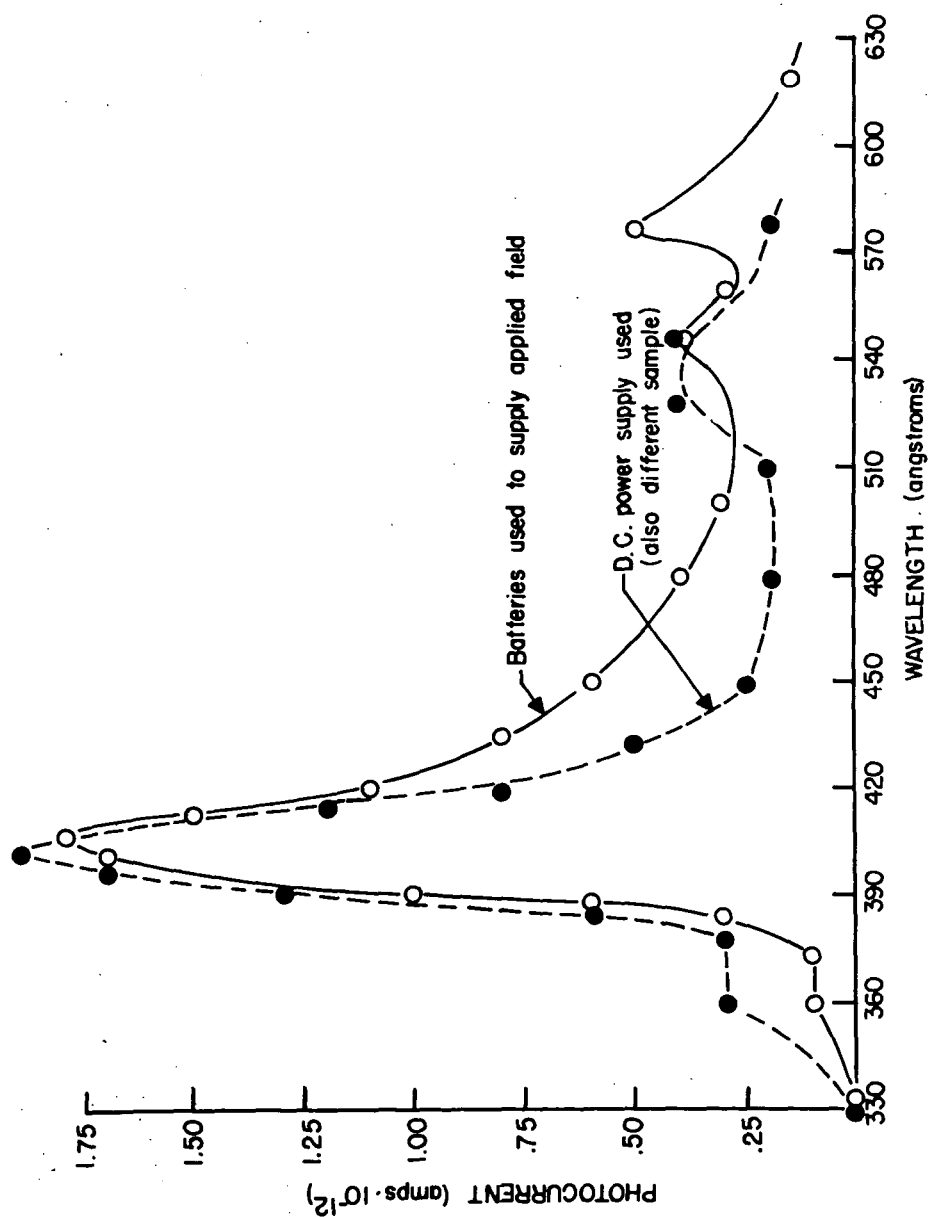


Figure 3. Photocurrent vs wave length for freshly dried colloidal lead azide.

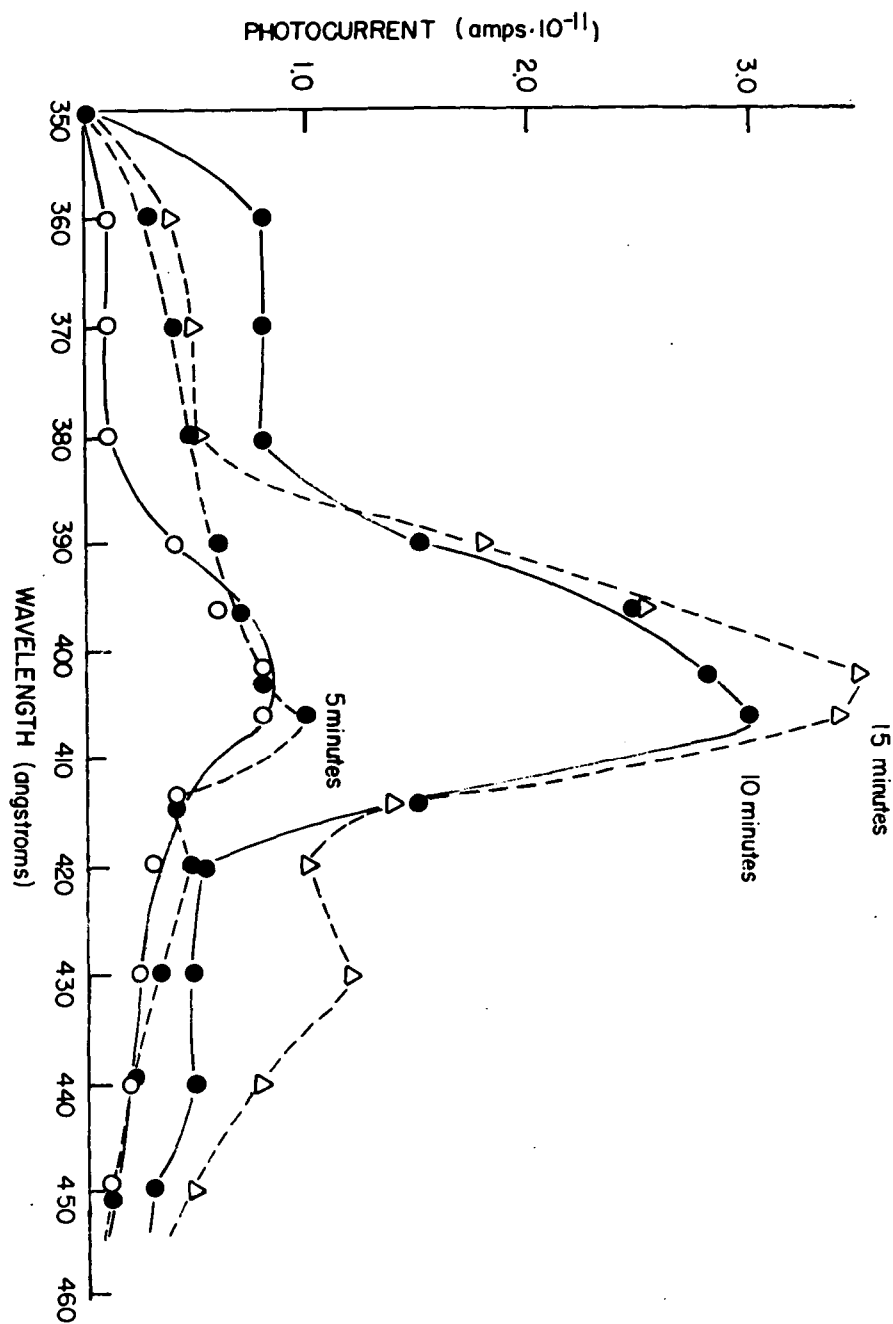


Figure 4a. Photocurrent vs wave length for colloidal Lead azide heated to 250°C.

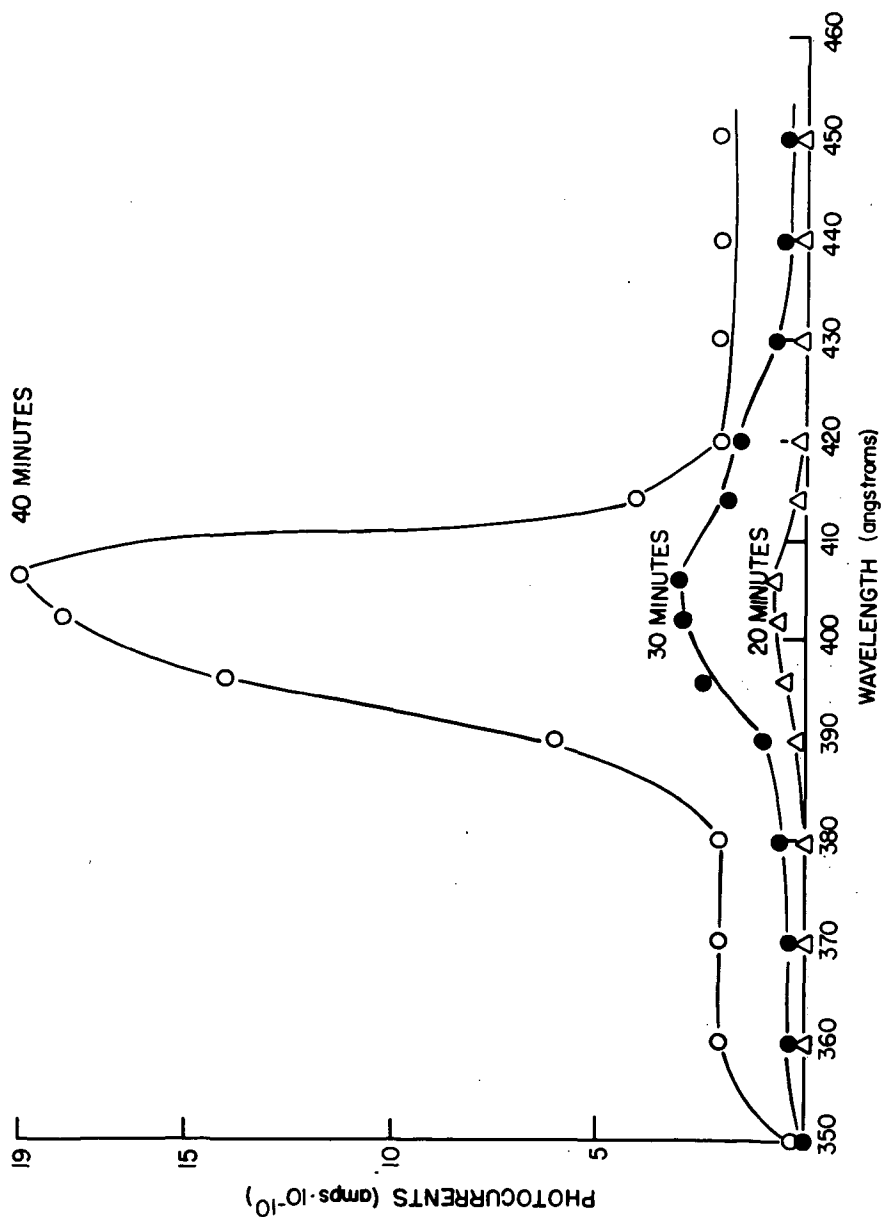


Figure 4b. Photocurrent vs wave length for colloidal lead azide heated to 250°C for extended periods:

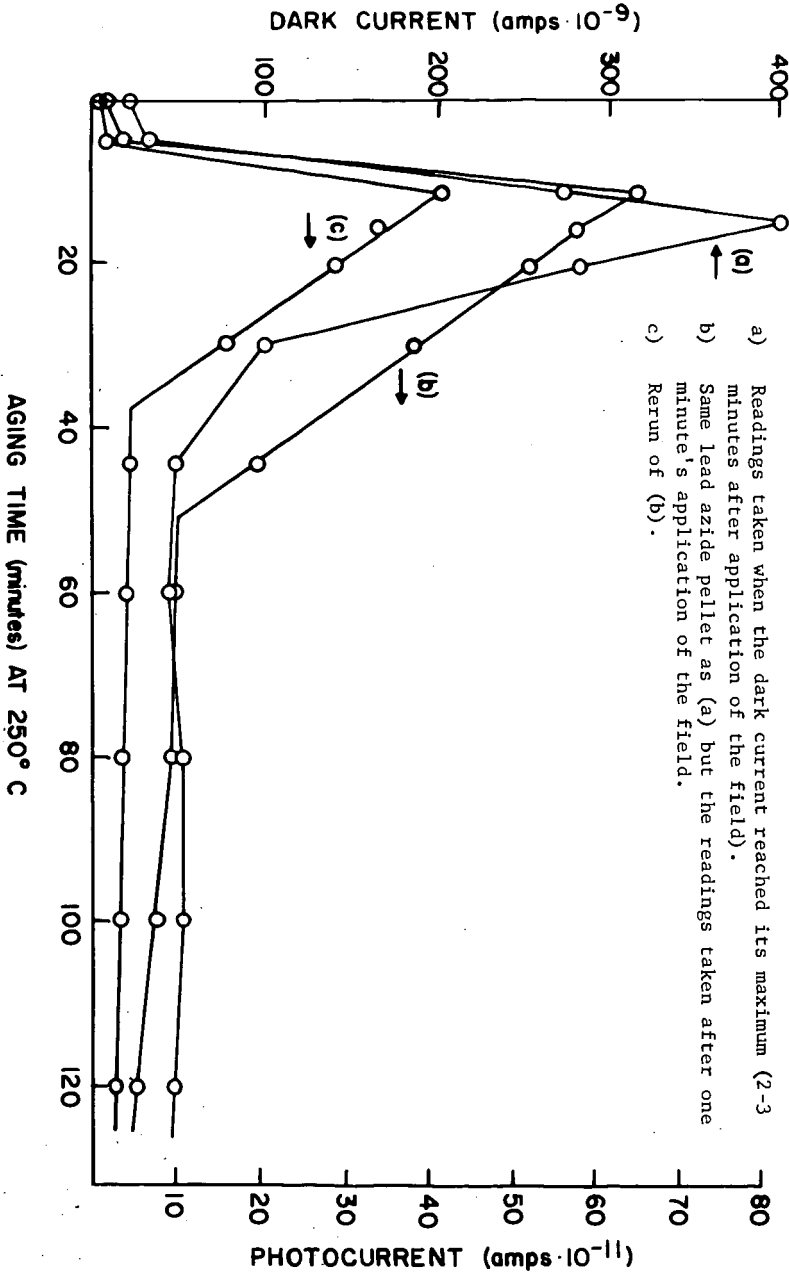


Figure 5. Dark current vs heat-treatment time at 250°C

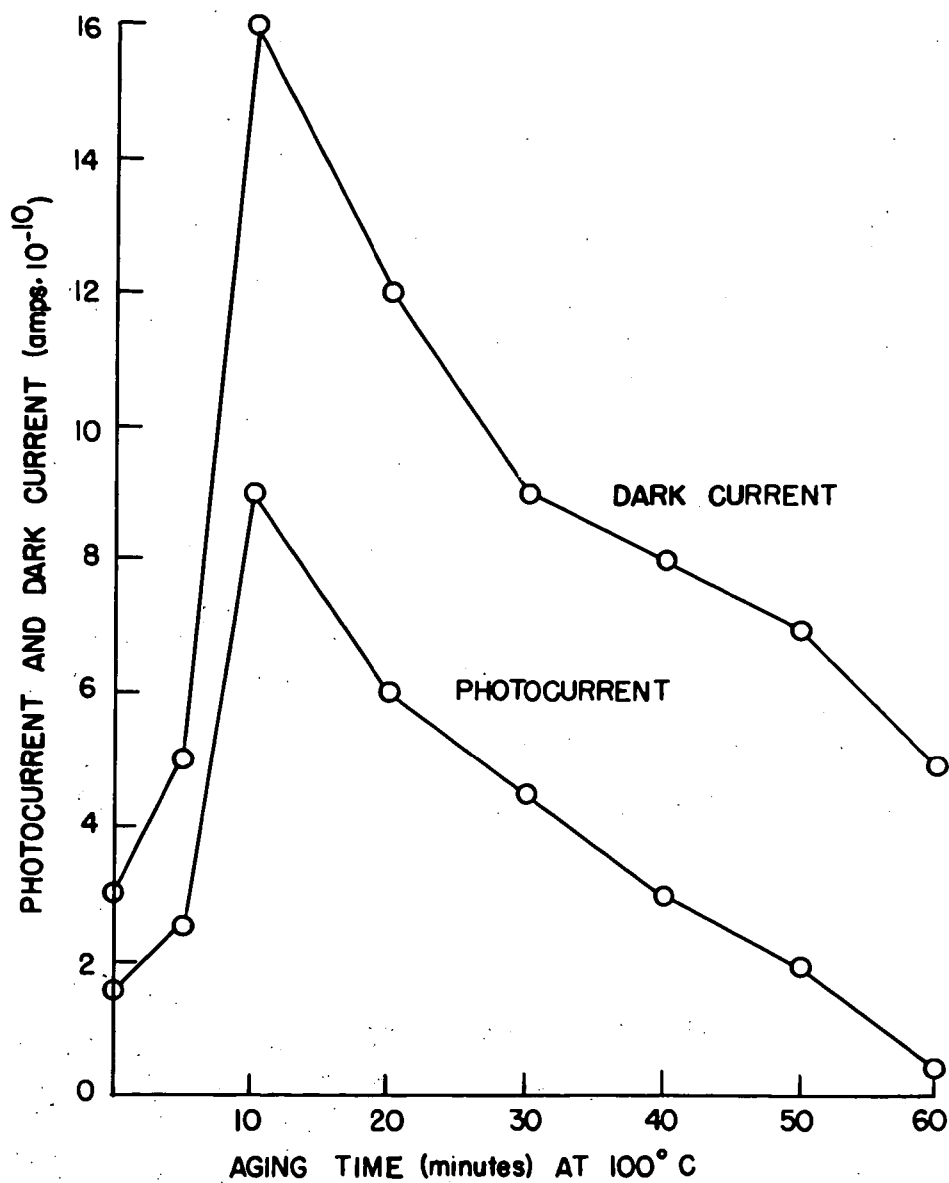


Figure 6. Photocurrent and dark current vs treatment time at 100°C.



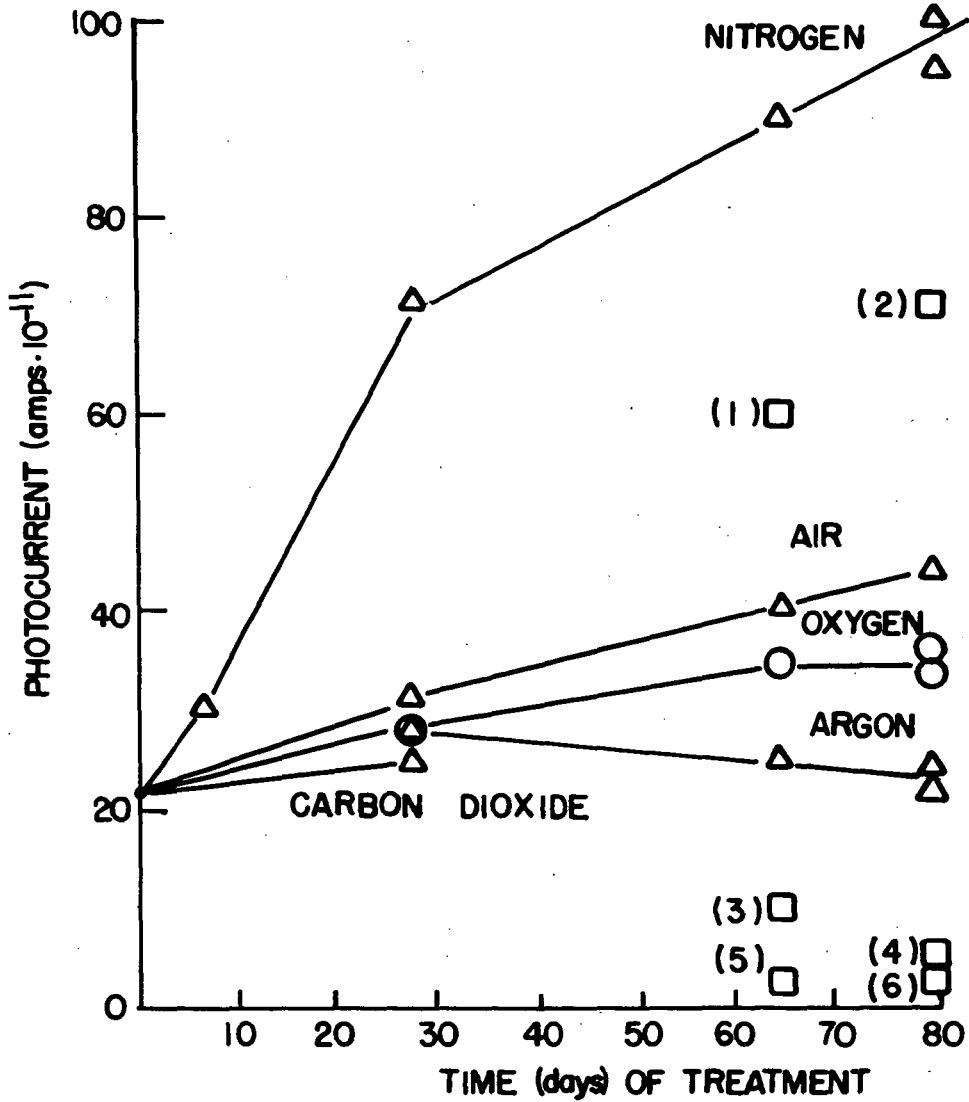


Figure 7. Photocurrent vs storage time in various gases at 35°C.